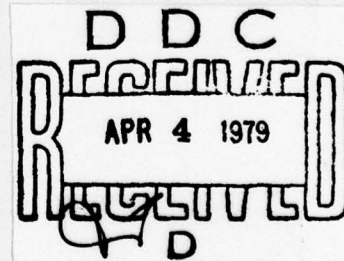| OF |
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SECOND-HARMONIC GENERATION OF THE NEODYMIUM
OPTICAL QUANTUM LASER BY CRYSTALLINE
POWDERS OF ORGANIC COMPOUNDS

by

E. O. Tykhonov and M. T. Shpak

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The study of new, nonlinear optical materials is an important problem in expanding practical applications of methods and equipment of quantum electronics. Also, physical information obtained during studies of the second-harmonic generation makes it possible to clarify some macroscopic optical properties of crystals and, in particular, to determine the coefficients of the tensor of nonlinear susceptibility of third rank.

It should be noted that finding promising nonlinear optical materials is aided to some degree by studies in piezo-electricity. The powder methods for identifying piezo-electric compounds, first proposed in Reference [1] were successfully developed, thus making possible the use of a number of search criteria in identifying about 500 compounds having a piezo effect [Refs. 2, 3]. The use of the powder method in nonlinear optics for studies of nonlinear optical materials was first reported in References [4] and [5] The thorough research of Reference 6 contains the results of studying second-harmonic generation of a large group of inorganic materials through the use of powder methods.

In recent communications [Refs. 7, 8], major attention is devoted to the mechanism that determines the magnitude of the nonlinear coefficients of a number of organic compounds.

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* English summary deleted

The present paper shows the results of investigative research for new nonlinear optical materials within the broad group of complex organic materials -- dyes, and several compounds used as starting products for the synthesis of dyes.

Prospects for use of molecular crystals of complex organic compounds as non-linear optical materials rest on a number of properties attributed to such crystals.

The intensity of the second harmonic is indicated by the magnitude of the tensor of the nonlinear susceptibility of third rank

$$I^{2\omega} \sim \chi_{ij}(2\omega) = \begin{pmatrix} d_{11} & d_{12} \cdots & d_{16} \\ d_{21} & \cdots & d_{26} \\ d_{31} & \cdots & d_{36} \end{pmatrix} \tag{1}$$

The elements d_{ij} of this matrix, which represent this tensor, have to be non-zero and as large as possible [Ref. 9]. On the other hand, by using the model of an anharmonic oscillator, it is possible to determine factors that influence the magnitude of the nonlinear coefficients [Ref. 9],

$$\chi_{ij}(2\omega) = \frac{N_0 \left(\frac{e^3}{m^2}\right) v}{D^2(\omega) D(2\omega)} \tag{2}$$

Here, N_0 is the average value of the density of optical electrons, $D(\omega) = \omega_0^2 - \omega^2 - i\Gamma\omega$ are the dispersion terms, and v is the coefficient of the term, which indicates the quadratic nonlinearity.

The piezo-electric tensor is non-zero for the following 20 non-centro-symmetric crystallographic classes: 1, 2, m, 222, mm2, 4, $\overline{4}$, 422, 4mm, $\overline{4}2$m, $\overline{4}3$m, 23, 3, 32, 3m, 6, 6mm, 622, $\overline{6}$, 6m2 [Ref. 10]. Generation of a second-harmonic is not possible for the two crystallographic classes, 422 and 622, according to the additional conditions of Kleinman symmetry [Ref. 11]. In most cases, the complex low-symmetric organic molecules form crystals of the three lower syngonies, with a large percentage of them forming non-centro-symmetric crystallographic classes (for molecules

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with a proper symmetry of 1, 2, m, mm, 222, the most probable Feodor [term unknown] groups are, according to the principle of tight packing, $\overline{P1}$, $P2_1$, $P2_1/c$, Pca, Pna, $P2_1 2_1 2_1$ [Ref. 12]).

The linear polarization of molecules with a large number of conjugate π-electrons, which include an overwhelming majority of dye compounds, is several times larger than the polarization of simple molecules. If account is taken of the dense packing of the molecular crystals, this phenomenon leads to a significant magnitude of $\chi_{ij}(2\omega)$ as a result of increasing N_0 (Equation 2). This result is known as Miller's Law [Ref. 13], according to which substances with a large coefficient of refraction are characterized by large values of coefficients of nonlinear susceptibility.

With a small exception, optics of dyes in the crystalline state and optics of complex organic compounds have not been investigated using the still-unsolved approach of growing large, single crystals of such compounds. Some data on the dispersion of the index of refraction have been obtained by studying poly-crystal and amorphous films of dyes on substrata. For amorphous films of dyes such as quinoline blue, brilliant green, malachite green, crystal violet, and rhodamine, which belong, respectively, to the cyanine, triphenylmethane, and xanthene chemical classes of dyes, the index of refraction changes from 1.5 in the transparent region to 2-2.5 in the region of absorption [Refs. 14, 15]. Although there is no basis for transferring these data to the crystalline state, they give a hint about some mean value of the index of refraction of molecular crystals of complex organic compounds. In accordance with Miller's Law, this assures values of basic elements equivalent to those for the better piezo-electric compounds already investigated, because

$$d_{ij} \sim (n^2 - 1)^3 \tag{3}$$

Another property of molecular crystals, which contributes to the effective second harmonic generation, arises from conditions of synchronism. As is known, the energy that is pumped into the electromagnetic wave due to the dispersion of phase velocities at/double the frequency for a nonlinear polarized medium and changes with the distance l as follows [Ref. 9]:

$$W(2\omega) = 2\omega \operatorname{Im} E(2\omega) P^{NL} \exp[i(\vec{k}_2 - 2\vec{k}_1)l], \tag{4}$$

where $\vec{k}_1$, $\vec{k}_2$ are the wave vectors of the electromagnetic wave in the medium. There will be no oscillations in the direction for which $\vec{k}_2 = 2\vec{k}_1$ and l can be taken as an arbitrary value. Crystals of the three lower syngonies, which are characteristic for organic dyes, are bi-axial. Even without considering the dispersion of indices for coefficients of refraction, which is characteristic of dye crystals [Ref. 16], the number of possible directions of synchronism for both types of phasing

$$(\Theta(I) - n^{o,e}(2\omega) = n^{e,o}(\omega) \quad \Theta(II) - n^{o,e}(2\omega) = \frac{1}{2}[n^{e,o}(\omega) + n^{o,e}(\omega)]) \tag{4a}$$

is very large [Ref. 17].

Observation and recording of the second-harmonic of a neodymium optical quantum laser due to powders of organic compounds were carried out using an experimental facility whose schematic is shown in the diagram. The neodymium optical quantum laser using a passive control of the figure of merit generated impulses with a power of 20 megawatts (using KQSS-7 glass, in the region of nonsynchronized modes). Laser radiation filtered by an infrared IKS-1 filter was directed without focusing onto the sample consisting of a dye powder between two glass plates located in front of

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the entrance slit of an SPM-2 monochromator. The FEU-38 photomultiplier using a head-on photo cathode was located at the exit slit of the monochromator. An SZS-16 light filter keeps the power radiation at 1.065 microns from entering the monochromator. The time constant of the electrical circuits of the photomultiplier and the C-1-13a oscillograph makes it impossible to resolve time, and a reading is made of the amplitude of the impulse on the screen of the oscillograph. Basic results of the research are shown in Tables 1 and 2, where l is the mean size of the kernel.

We should mention a shortcoming of the methodology in which use is made of powders not calibrated as to size. In the given case, information is lost about the conditions for synchronism in the material being studied, and the evaluation of the corresponding efficiency *second harmonic generation* is approximate.

In all cases where it was possible to compare positive or negative results from the second-harmonic generation with data from x-ray analysis or with information of the piezo-effect, such comparisons were made. In an overwhelming majority of cases there were no contradictions, in some cases contradiction is obvious, and in others the absence of the second-harmonic is caused by other circumstances than the factor of central symmetry.

[3?]

The absence of second-harmonic generation in azobenzene (No. 2/in Table 1) agrees with data from x-ray analysis but contradicts results of studies of the piezo-effect. Apparently, the powder method of second-harmonic generation is a convenient, practical method for obtaining data about the presence or absence of a center of symmetry in a crystal considering dimensions dictated by particulars of the tensor of nonlinear susceptibility for groups 422, 622, and 432. In some materials (azenaphthene, No. 17 [19?] in Table 1), no second-harmonic generation is observed, in spite of the fact that the tensor of third rank is non-zero. If data on the Feodor group of crystals used are correct, analogous cases are of

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interest for the explanation of causes for the absence of second-harmonic generation. It should be emphasized that conclusions can be valid only if the history of the powder being investigated is known. Thus, in the case of benzophenone (No. 3 [4?] in Table 1), there is no second-harmonic generation if the powder is obtained from a molten material that is later cooled; the same powder obtained from solution will generate an intensive harmonic. The most likely causes for this are phase transition and the amorphous state of the material.

The compounds listed in Table 1, in the majority of cases, are the starting products for obtaining chemically more complex, deeply dyed compounds. Thus, Nos. 35 and 36 in Table 1, which are "half" molecules absorbing in the region of 7700 Angstroms, are isomorphous and probably have the same history. However, the harmonic is generated by only one of them. An analogous result is obtained for isomorphic compounds of benzotriazole and benzimidazole (Nos. 40 and 41 in Table 1).

The choice of substances for research was based on the genetic principle, from which it follows that if there is at least one compound among a number of compounds having similar chemical structures with piezo-effect, then the whole group is potentially piezo-active [Ref. 3].

In the structural plan, this principle arises from the principle of invariance within Feodor groups for isomorphic and homologous isomorphic molecules [Ref.t 12]. The imprecision of these criteria in the general case is well known; in the case of optically nonlinear substances, it is apparent from the data in Tables 1 and 2.

Because second-harmonic generation depends on the history of the samples, research into specific cases used recrystallization. The powder generating the second-harmonic of the brilliant green [dye] was dissolved in ethanol and then films were obtained by evaporating the solvent by heating the substrata. The films were mirror-like, which attests to their amorphous structure [Ref. 14]. No harmonics were

generated by these samples. As time passed, the formation of crystallization centers was observed at separate locations of the glass surface of the film. Such samples generate harmonics in the places where crystallic centers are created. After some additional time, the entire film becomes dull (that is, crystalline) and generates harmonics uniformly across the surface.

Other materials (aniline blue and eriohlausin [term unknown] in Table 2) whose molecular structure is more complex do not crystallize under similar conditions. It is possible that in some cases for complex nonsymmetric dye molecules the amorphous state is more advantageous from an energy point of view. However, before a particular compound is assigned to the category of noncrystallizing, other research on conditions of crystallization has to be done. For some dyes of similar molecular structure (for example, water blue, Table 2), the piezo-electric tensor is non-zero.

An example of contradictory data analogous to the above example of azobenzene is the behavior of indigo-carmine (Table 2).

The large group of oxy-, tia-, and azo-dyes shown in Table 2 obviously belongs to the category of centro-symmetrical compounds.

A group of thalocyanine dyes also belongs to the centro-symmetrical compounds. In this class of dyes, there are no contradictions among data of x-ray structural analysis, piezo-effect, or second-harmonic generation.

Second-harmonic generation by cyanine dyes is observed only in specific cases (Nos. 33 and 40, Table 2).

In studying the broad group of substances, no second-harmonic generation was observed in the region of the absorption band of the second harmonic. Studies of substances, however, that have absorption at the fundamental frequency are made difficult by thermal destruction.

In both cases, an increase in nonlinear susceptibility should be observed, in accordance with Equation 2. Inasmuch as the second harmonic is not observed in the

region of absorption bands of a number of compounds whose piezo-electric tensor is known to be non-zero (Nos. 13, 26, and 27, Table 2), we can conclude that an increase in $\chi_{ij}(2\omega)$ due to resonance does not compensate for the active absorption of radiation at the second harmonic.

Besides in the nonlinear optical materials listed in Table 1, whose second-harmonic generation efficiency is no worse (in particular cases) than that of the best nonlinear materials used, second-harmonic generation was observed in a group of optically active compounds, such as d-galactose, d-dextrose, cane sugar, sulphate of quinidine, and others.

Powder methodology thus in large degree solves the problem of finding nonlinear optical materials with large nonlinear coefficients. Those among them whose single crystals can be grown without large technological difficulties might prove practical for utilization. Primarily, such single crystals are relatively simple molecular compounds such as benzophenone, xanthone, benzomidazole, resorcinol, m-nitrobenzaldehyde, and others.

On the other hand, the demands of quantum electronics could stimulate research in the growth of single crystals and more complex compounds such as derivatives of anthraxynone, benzathrone, triphenylmethane, and 2-(p-nitrosterol)-xinoline.

In conclusion, the authors express their gratitude to colleagues at the Institute for Organic Chemistry of the Academy of Sciences of the Ukrainian SSR, H. H. Dyadyushi and O. O. Shulezhko, and also to their colleague at the Chernivets' State University, E. P. Opanasenko, who contributed to the research on a number of compounds.

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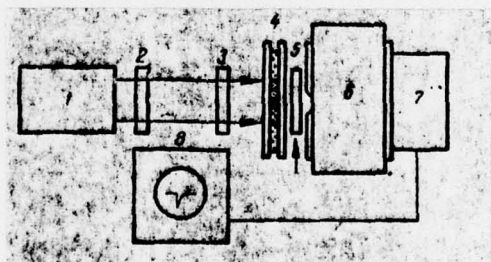
Figure

Key:
1. Optical quantum laser
2, 3, 5. Light filters
4. Sample
6. Monochromator
7. FEU-38 photomultiplier
8. Oscillograph

Table 1.

Порошки органічних сполук з $\lambda_{пога} \leqslant 0,535$ мк

(b) Номер зразка	(c) Сполука	(d) Загальна характеристика	(e) Група симетрії (f) молекула	(e) Група симетрії (g) кристал	(h) Відносна інтенсивність ДГ $J^{2\omega}/J(\text{LiNbO}_3)$	(i) Очевидна причина відсутності ГДГ	(j) Імовірна причина відсутності ГДГ	(k) Примітки
1	антрацен	кристалічний порошок, одержаний сублімацією; $l \sim 0,5$ мм	mmm	$\frac{2}{m}$ [12]	0	$d^{2\omega}_{ij}=0$	—	аналогічний результат для 2,3-диметилантрацену; 9,10-диброматрацену
2	3,4-Ас-1,2-бенз-антрацен	жовтий порошок, $l \leqslant 100$ мк	m	?	0,05	—	—	—
3	азобензол: цис-, транс-	порошок червонувато-жовтого кольору, $l \leqslant 0,5$ мк	$mm, 2$ $\frac{2}{m}$	mmm $\frac{2}{m}$ [12]	0	$d^{2\omega}_{ij}=0$	—	$d_{ij} \neq 0$ [2]
4	бензофенон	прозорий порошок, $l \leqslant 0,5$ мм	$mm, 2, 1$	222 [18]	0,1	—	—	—
5	ксантон	жовтуватий порошок, $l \leqslant 100$ мк	$mm, 2, 1$	?	0,1	—	—	—
6	дифеніл	білий порошок, $l \leqslant 100$ мк	mmm	$\frac{2}{m}$ [12]	0	$d^{2\omega}_{ij}=0$	—	—
7	дифеніламін	кристалічний порошок, $l \leqslant 1$ мм	?	?	0	—	$d^{2\omega}_{ij} < d^{2\omega}_{ij}$ кварц	$d_{ij} \neq 0$ [2]
8	коронен	порошок жовтого кольору, $l \leqslant 0,5$ мм	$\frac{6}{mmm}$	$\frac{2}{m}$ [12]	0	$d^{2\omega}_{ij}=0$	—	—
9	антрахінон	жовтий порошок, $l \leqslant 100$ мк	mmm	$\frac{2}{m}$ [12]	0	$d^{2\omega}_{ij}=0$	—	—
10	1-метоксіантрахінон	» »	?	?	0,1	—	—	—
11	1-етоксіантрахінон	» »	?	?	0,5	—	—	—
12	1,2-бензантрахінон	» »	m	?	0	—	$d^{2\omega}_{ij}=0$	—
13	α-нітроантрахінон	» »	?	?	0	—	$d^{2\omega}_{ij}=0$	—
14	бензантрон	» »	m	?	0,4	—	—	—
15	3-метоксибензантрон	» »	m	?	0,1	—	—	—
16	3-бромбензантрон	» »	m	?	1,0	—	—	—
17	азулен	темносиній порошок, $l \leqslant 0,5$ мм	mm	?	0	—	поглинання на 2ω	—
18	фенантрен	білий порошок, $l \leqslant 0,5$ мм	m	?	0	—	$d^{2\omega}_{ij}=0$	—

Keys: (a) Powders of organic compounds with $\lambda_{absorption} \leqslant$ 0.535 micron; (b) sample number; (c) Compound; (d) General characteristics; (e) Symmetry group; (f) Molecule; (g) Crystal; (h) Relative intensity of the second harmonic; (i) Apparent reason for absence of the second-harmonic generation; (j) Probable reason for absence of the second-harmonic generation; (k) Comments; (1c) Anthracene; (1d) Crystalline powder obtained by sublimation; (1k) Analogous results for: 2, 3 - dimethylanthracene and 9, 10 - dibromoanthracene; (2c) 3, 4, As - 1, 2 - benzanthracene; (2d) - Yellow powder; (3c) Azobenzene: cis -, trans - (3d) Powder of reddish-yellow color; (4c) Benzophenone; (4d) Transparent powder; (5c) Xanthone; (5d) Yellowish powder; (6c) Diphenyl; (6d) White powder; (7c) Diphenylamine; (7d) Crystalline powder; (7j) Quartz; (8c) Coronene; (8d) Powder of yellow color; (9c) Anthraquinone; (9d) Yellow powder; (10c) 1-methoxyanthraquinone; (11c) 1-ethoxyanthraquinone; (12c) 1, 2-benzanthraquinone; (13c) α-nitroanthraquinone; (14c) Benzanthrone; (15c) 3-methoxybenzanthrone; (16c) 3-bromobenzanthrone; (17c) Azulene; (17d) Dark-blue powder; (17j) Absorption at 2ω; (18c) Phenanthrene; (18d) White powder.

Table 1. Continued.

| №	(c)	(d)	mm	mm [12]		?		
19	аценафтен	білий порошок, l≤1 мм	mm	mm [12]	0	?	$d_{ij}^{2\omega} < d_{ij}^{2\omega}$ кварц	—
20	дифенілстирилпіразолін	жовтий порошок, l≤100 мк	?	?	1,0	—	—	—
21	N-фенілхінолій йодид	жовтий порошок, l≤100 мк	?	?	0	—	—	—
22	N-феніл-6-етоксихінолій перхлорат	світлосірий порошок, l≤100 мк	?	?.	0,1	—	поглинання на 2ω	—
23	рубіцен	кристалічний порошок, l≤1 мм	?	?	0	—	—	—
24	3-нітрокарбазол	жовтий порошок, l≤100 мк	?	?	0,05	—	—	—
25	флуорен	білий порошок, l≤200 мк	?	?	0	—	$d_{ij}^{2\omega}=0$	—
26	флуоренон	кристалічний порошок, l≤1 мм	?	?	0	—	$d_{ij}^{2\omega}=0$	—
27	параоксифенетол	жовто-оранжовий порошок, l≤1 мм	?	?	0	—	$d_{ij}^{2\omega}=0$	—
28	азоксибензол	кристалічний порошок жовтого кольору, l≤0,5 мм	?	?	0	—	$d_{ij}^{2\omega}=0$	—
29	2-(p-нітростирил)-хінолін	жовтий порошок, l≤100 мк	?	?	0,5	—	—	—
30	2-(p-нітрофенілацетиленіл)хінолін	жовтий порошок з оранжовим відтінком, l≤100 мк	?	?	0	—	$d_{ij}^{2\omega}=0$	—
31	2-(p-диметиламінофенілацетиленіл)-хінолін	кристалічний порошок оранжового кольору, l≤1 мм	?	?	0	—	$d_{ij}^{2\omega}=0$	—
32	2-(p-диметиламіностирил)-хінолін	оранжовий порошок, l≤100 мк	?	?	0,5	—	—	—
33	2-фенацилхінолін	жовтооранжовий порошок, l≤100 мк	?	?	0,2	—	—	—
34	азоксианізол	кристалічний порошок жовтого кольору, l≤0,5 мм	?	?	0	—	$d_{ij}^{2\omega}=0$	—
35	біс(5-бензтіазоліл-2)тієніл-2]метандиетилбромід	порошок жовтого кольору (ниткоподібний), l≤100 мк	?	?	0,5	—	—	—
36	біс(5-(бензтіазоліл-2)фурил-2]метандиетилбромід	» » »	?	?	0	—	$d_i^{2\omega}=0$	—
37	S-окис-3,6-динітрофентіазин	кристалічний порошок жовтого кольору, l≤1 мм	?	?	0,05	—	—	—
38	акридин	сірий порошок, l≤100 мк	?	?	0	—	$d_{ij}^{2\omega}=0$	—
39	уротропін	білий порошок, l≤100 мк	?	?	0,1	—	—	$d_{ij}=0$ [2]

Keys: (Continued) (19c) Acenaphthene; (19d) White powder; (19j) Quartz; (20c) Diphenylstyrylpyrazoline; (20d) Yellow powder; (21c) N-phenylquinoline iodide; (21d) Yellow powder; (22c) N-phenyl-6-ethoxyquinoline perchlorate; (22d) Light-gray powder; (23c) Rubicene; (23d) Crystalline powder; (23j) Absorption at 2ω; (24c) 3-nitrocarbazole; (24d) Yellow powder; (25c) Fluorene; (25d) White powder; (26c) Fluorenone; (26d) Crystalline powder; (27c) Paraoxyphenetole; (27d) Yellow-orange powder; (28c) Azoxybenzene; (28d) Crystalline powder of yellow color; (29c) 2-(p-nitrostyryl)-quinoline; (29d) Yellow powder; (30c) 2-(p-nitrophenylacetylenyl) quinoline;(30d) Yellow powder with an orange tint; (31c) 2-(p-dimethylaminophenytacetylene)-quinoline; (31d) Crystalline powder of yellow color; (32c) 2-(p-dimethylaminostyryl) quinoline;(32d) Orange powder; (33c) -2-phenacyl quinoline; (33d) Orange-yellow powder; (34c) Azoxyanisole; (34d) Crystalline powder of yellow color (35c) Bis-[5-(benzthiazolyl-2) thienyl-2] methanediethylbromide; (35d) Powder of yellow color (thread-like); (36c)   -[5-benzthiazolyl-2) furyl-2] methanediethylbromide; (37c) S-oxy-3, 6 - dinitrophenthiazine; (37d) Crystalline powder of yellow color; (38) Acridine; (38d) Gray powder; (39c) Urotropine; (39d) White powder.

Номер зразка	(c) Сполука*	(d) Загальна характеристика**	Група симетрії		Відносна інтенсивн. ДГ. $\frac{J^{2\omega}}{J^{2\omega}(Li\,NbO_3)}$	Очевидна причина відсутності ГДГ	Імовірна причина відсутності ГДГ	(к) Примітки
			молекула	кристал				
40	бензотріазол	кристалічний порошок, $l \leqslant 1$ мм	m	?	0	--	$d_{ij}^{2\omega} = 0$	ізоморфний піаселенол, належить до групи *Pna* [12]
41	бензимідазол	кристалічний порошок, прозорий, $l \leqslant 2$—3 мм	m	?	0,05	—	—	—
42	трифенілметан	Те ж, $l \leqslant 0,3$ мм	—	?	0	—	—	—
43	трифенілкарбінол	», $l \leqslant 0,3$ мм	—	?	0	$d_{ij} = 0$	—	діокситрифенілкарбінол, має $d_{ij} \neq 0$ [2]
44	м-нітробензальдегід	білий порошок з жовтим відтінком, $l \leqslant 100$ мк	?	?	0,5	—	—	—
45	резорцин	прозорий порошок з оранжовим відтінком, $l \leqslant 100$ мк	?	[12]	0,2	—	—	—

(46) * Нижче наведені формули маловідомих сполук.
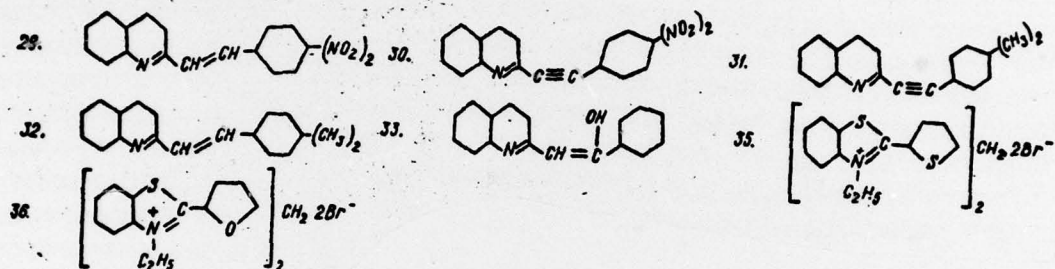
Keys: Continued. (40c) Benzotriazole; (40d) Crystalline powder; (40k) An isomorphous piaselenole, belongs to the Pna-group (Ref. 12); (41c) Benzimidazole; (41d) Transparent crystalline powder; (42c) Triphenylmethane; (42d) Triphenylmethane; (43c) Triphenylcarbinol; (43d) Triphenylcarbinol; (43k) Dioxytriphenyl carbinol with $d_{ij} \neq 0$ (Ref. 2); (44c) m-nitrobenzaldenhyde; (44d) White powder with yellow tint; (45c) Resorcin; (45d) Transparent powder with orange tint; (46) *Formulas for lesser known compounds are shown below.

Table 2.

Порошки органічних сполук з $\lambda_{погл} > 0,535$ мк

Номер зразка	Сполука, клас°	Загальна характеристика	Максимум молекулярного поглинання (Å), розчинник	Група симетрії кристала	Відносна інтенсивність ГДГ $\frac{I_{2\omega}}{I_{2\omega}(\text{LiNbO}_3)}$	Очевидна причина відсутності ГДГ	Імовірна причина відсутності ГДГ	Примітки
1	бромфеноловий синій (трифенілметановий)	темносиній порошок з металевим блиском, $l \leqslant 200$ мк	5850, H_2O	?	0	?	?	—
2	водний голубий (трифенілметановий)	сироголубий порошок, $l \leqslant 1$ мм	5800, H_2O	нецентросиметричний	0	—	поглинання на 2ω	$d_{11} \neq 0$ [2]
3	еріоглауцин «А» (трифенілметановий)	темнозелений порошок, $l \leqslant 100$ мк	6300, H_2O	?	0	—	аморфність	—
4	фенолфталеїн	білий порошок, $l \leqslant 100$ мк	—	—	0,05	—	—	—
5	етиловий фіолетовий (трифенілметановий)	зеленуватий порошок, $l \leqslant 100$ мк	5950, CH_3CH_2OH	?	0	—	аморфність	—
6	аніліновий синій (трифенілметановий)	темний порошок, $l \leqslant 100$ мк	5800, H_2O	?	0	—	аморфність або поглинання на 2ω	—
7	метиловий зелений (трифенілметановий)	темнозелений порошок, $l \leqslant 100$ мк	6280, H_2O	?	0,05	—	—	—
8	малахітовий зелений (трифенілметановий)	темнозелений порошок, $l \leqslant 0,5$ мм	6400, CH_3CH_2OH	?	1,0	—	—	—
9	брильянтовий зелений (трифенілметановий)	»	6420, CH_3CH_2OH	?	1,0	—	—	—
10	аурамін (дифенілметановий)	—	4200, CH_3CH_2OH	—	0,1	—	—	$d_{ij} \neq 0$ [7]
11	1,3 - біс(р - диметиламінофеніл)-триметинціанінперхлорат (дифенілметановий)	зелений порошок з металевим блиском, $l \leqslant 100$ мк	6940, CH_3CH_2OH	?	0	$d_{ij}^{2\omega} = 0$	—	—
12	індигокармін (індигоїдний)	темнофіолетовий порошок, $l \leqslant 100$ мк	6100, H_2O	$\frac{4}{m}$ [19]	0	$d_{ij}^{2\omega} = 0$	—	$d_{11} \neq 0$ [2]
13	нафтазарин (нафтазариновий)	»	5500, H_2O	?	0	—	поглинання на 2ω	$d_{11} \neq 0$ [2]

Key: (a) Powders of organic compounds with $\lambda_{absorption} >$ micron
(b) Sample number, (c) Compound, class; (d) General characteristics;
(e) Maximum of the molecular absorption (in Å), solvent; (f) Symmetry
group of the crystal; (g) Relative intensity of second-harmonic
generation; (h) Apparent reason for absence of second-harmonic
generation, (i) Probable reason for absence of second harmonic genera-
tion; (j) Comments; (1c) Bromonphenol blue (triphenyl-methane);
(1d) Dark-blue powder with metallic luster; (2c) Water-blue (tri-
phenylmethane); (2d) Gray-blue powder; (2f) Non Centro-symmetric; (2i)
Absorption at 2ω, (3c) Erioglaucine A (triphenylmethane);(3d) Dark-
green powder; (3i) Amorphism; (4c) Phenolphthalein; (4d) White powder;
(5c) Ethyl violet (triphenylmethane); (5d) Greenish powder;
(5i) Amorphism; (6c) Aniline blue (triphenylmethane); (6d) Dark powder;
(6i) Amorphism or absorption at 2ω, (7c) Methyl green (triphenylmethane)
(7d) Dark-green powder; (8c) Malachite green (triphenylmethane);
(8d) Dark-green powder; (9c) Brilliant green (triphenylmethane);
(10c) Auramine (diphenylmethane); (11c) 1, 3 - bis(p-dimethylamino-
phenyl)-trimethinecyanineperchlorate (diphenylmethane); (11d) Green
powder with metallic luster; (12c) Indigo-carmine (indigoid); (12d)
Dark-violet powder; (13c) Naphthazarine; (13i) Absorption at 2ω.

№	(c)	(d)	(e)				(i)	(j)
14	галламін синій (оксазиновий)	сіроголубий порошок, $l \leqslant 300$ мк	6100, CH_3CH_2OH	?	0	—	$d^{2\omega}_{ij}=0$, належить до групи $\frac{2}{m}$	—
15	резазурин (оксазиновий)	темнофіолетовий порошок, $l \leqslant 200$ мк	6020, H_2O	?	0	—	$d^{2\omega}_{ij}=0$	—
16	метиленовий синій (Азур-1) (тіазиновий)	темнозелений порошок, $l \leqslant 200$ мк	6670, H_2O	$\frac{2}{m}$ [20]	0	$d^{2\omega}_{ij}=0$		—
17	азур-2 (тіазиновий)	,,	6570, CH_3CH_2OH	?	0	—	$d^{2\omega}_{ij}=0$, внаслідок належності до $\frac{2}{m}$	—
18	метиленовий голубий (тіазиновий)	темнозелений порошок, $l \leqslant 100$ мк	6650, H_2O	$\frac{2}{m}$ [20]	0	$d^{2\omega}_{ij}=0$	$d^{2\omega}_{ij}=0$	
19	антраценовий голубий (антрахіноновий)	темносиній порошок, $l \leqslant 100$ мк	5800	?	0	—	$d^{2\omega}_{ij}=0$	—
20	зелений Біндшедлера (хіноніміновий)	темнофіолетовий порошок	7200, нітрометан	?	0	—	аморфність або $d^{2\omega}_{ij}=0$	—
21	трипановий синій (дисазобарвники)	синій порошок, $l \leqslant 1$ мм	—	?	0	—	аморфність	—
22	дианіловий синій (дисазобарвники)	темний порошок, $l \leqslant 100$ мк	6000, H_2O	?	0	—	аморфність	—
23	варіамін синій В (моноазобарвники)	синій порошок, $l \leqslant 0,5$ мм	—	?	0	—	$d^{2\omega}_{ij}=0$	—
24	N-етилфеназин (азиновий)	чорний порошок, $l \leqslant 100$ мк	7100, CH_3CH_2OH	?	0	—	аморфність або $d_{ij}=0$	—
25	п-нітрозодиметиланілін (нітрозобарвники)	зелений порошок, $l \leqslant 200$ мк	—	?	~ 0	—	$d^{2\omega}_{ij} < d^{2\omega}_{ij}$ кварц	$d_{ij} \neq$
26	еозин синюватий (ксантеновий)	темночервоний порошок, $l \leqslant 100$ мк	5200, H_2O	?	~ 0	—	поглинання на 2ω	$d_{ij} \neq 0$ [2]
27	флуоресцеїн (ксантенові)	червоний порошок, $l \leqslant 100$ мк	4940, H_2O	?	~ 0	—	$d^{2\omega}_{ij}=0$, оскільки імовірна кристалічна група $\frac{2}{m}$	$d_{ij} \neq 0$ [2]
28	Mg-фталоціанін (фталоціанінові)	темносиній порошок, $l \leqslant 200$ мк	6800, хінолін	?				ізоморфні молекули Ni-, Pt-фталоціанінів належать до федорівської групи $P2_1/a$ [12]

Key: (14c) Gallamine Blue (oxazine); (14d) Gray-blue powder; (14i) Belongs to the 2/m group; (15c) Resazurin (oxazine); (15d) Dark-violet powder; (16c) Methyl Blue (Azure - 1) (Thiazine); (16d) Dark-green powder; (17c) Azure-2 (thiazine); (17i) Due to belonging to the 2/m [-group]; (18c) Methyl Blue (thiazine); (18d) Dark-green powder; (19c) Anthracene Blue (anthraquinone); (19d) Dark-blue powder; (20c) Bindshedler's Green (quinonimine); (20e) Nitromethane; (20i) Amorphism or (21c) Trypan-Blue (disazo dye); (21d) Blue powder; (21i) Amorphism; (22c) Dianil Blue (disazo dye); (22d) Dark powder; (22i) Amorphism; (23c) Variamine Blue B (monoazo dye); (23d) Blue powder; (24c) N-ethylphenazine (azine); (24d) Black powder; (24i) Amorphism or $d_{ij}=0$

(25c) n-nitrosodimethylaniline (nitroso dye); (25d) green powder; (25i) quartz [subscript]; (26c) Eosine Bluish (xanthenes); (26d) Dark-powder; (26i) Absorption at 2ω; (27c) Fluorescein (xanthenes); (27d) Red powder; (28c) Mg-phthalocyanine (phthalo-cyanines); (28d) Dark-blue powder; (28e) Quinoline; (28i) Since crystalline group 2/m is probable; (28j) Isomorphous molecules of Ni-, and Pt-phthalocyanines belong to the Fedorov group $P2_{1/a}$ (Ref. 12).

✱ (20e) Nitromethane.

14

Номер зразка	(c) Сполука, клас	(d) Загальна характеристика	Максимум молекулярного поглинання (Å), розчинник	Група симетрії кристала	Відносна інтенсивність ГДГ $\frac{f_{2\omega}}{f_{2\omega}(\text{LiNbO}_3)}$	Очевидна причина відсутності ГДГ	(i) Імовірна причина відсутності ГДГ	(j) Примітка
29	Cu-сульфофталоціанін (фталоціанінові)	темносиній порошок з металевим блиском, $l \leqslant 200$ мк	—	?	0	—	$d_{ij}^{2\omega} = 0$	ізоморфні молекули Ni-, Pt- фталоціанінів належать до федорівської групи $P2_1/a$ [12]
30	пінавердол (ціаніновий)	темнофіолетовий порошок, $l \leqslant 200$ мк	5620, CH₃CH₂OH	?	0	—	поглинання на 2ω	—
31	хіноліновий синій (ціаніновий)	темно-синій порошок, $l \geqslant 0,5$ мм	5920, CH₃CH₂OH	?	0	—	$d_{ij} = 0$ або поглинання на 2ω	—
32	криптоціанін (ціаніновий)	темнозелений порошок з металевим блиском, $l \leqslant 200$ мк	7150, CH₃CH₂OH	?	0	—	$d_{ij}^{2\omega} = 0$	для гомологічно ізоморфного пінаціанолу $d_{ij} \neq 0$ [2]
33	1-етил-2[3-(1-етилхіноліліден)метилізоіндоліліден-1]метил-хіноліній йодид (ціаніновий)	темнозелений порошок, $l \leqslant 100$ мк	6785, CH₃CH₂OH	?	0,05	—	$d_{ij} = 0$ або поглинання на 2ω	—
34	3-3'-диметил-9,11(о-феніл-ен)-тіадикарбоціанін йодид	зелений порошок, $l \leqslant 200$ мк	7550, CH₃CH₂OH	?	0	—	?	—
35	біс(N-п-метоксифеніл-6-метоксихінолін-4)пентаметинціанінперхлорат (ціаніновий)	темнозелений порошок з металевим блиском, $l \leqslant 0,5$ мм	8330, ацетон	?	0	—	$d_{ij} = 0$	—
36	біс(2H-3-феніл-4-метил-1,4-бензоксазин)монометинціанінперхлорат (ціаніновий)	темнофіолетовий порошок, $l \leqslant 100$ мк	7340, CH₃CH₂OH	?	0	—	$d_{ij}^{2\omega} = 0$	—
37	3-3'-діетилтіатрикарбоціаніній йодид (ціаніновий)	темнозелений порошок з металевим блиском, $l \leqslant 200$ мк	7500, CH₃CH₂OH	?	0	—	$d_{ij}^{2\omega} = 0$	гомологічно ізоморфний тіокарбоціанін кристалізується в федорівську групу $P\bar{1}$ [21]

Key: (29c) Cu-sulphophthalocyanine (phthalocyanines); (29d) Dark-blue powder with metallic luster; (29j) [See under 28j above]; (30c) Pinaverdol (cyanine); (30d) Dark-violet powder; (30i) Absorption at 2ω; (31c) Quinoline Blue (cyanine); (31d) Dark-blue powder; (31i) ... or absorption at 2ω; (32c) Cryptocyanine (cyanine); (32d) Dark-green powder with metallic luster; (32j) For homologously isomorphic pinacyanol d_ij ≠0 (Reference 2); (33c) 1-ethyl-2[3-(1 ethylquinoliniliden) (methylisoindoliniliden-1] methyl-quinoline iodide.(cyanine); (33d) Dark-green powder; (34c) 3-3'-dimethyl-9, 11(o-phenylene)-thiadicarbocyanine iodide; (34d) Green powder; (35c) Bis(N-n-methoxyphenyl-6-methoxyquinoline-4)pentamethine-cyanineperchlorate (cyanine); (35d) Dark-green powder with metallic luster; (35e) Acetone; (36c) Bis(2H-3-phenyl-4-methyl-1, 4-benzoxazine) monomethine cyanineperchlorate (cyanine); (36d) Dark-violet powder; (37c) 3-3'-diethylthiatricarbo cyanineiodide (cyanine); (37d) Dark-green powder with metallic luster; (37j) Homologously isomorphic tiocarbocyanine crystalizes into the Fedorov group P1 [Ref. 21].

38	біс(1-метилтіазоло[2,3-C][1,4]бензоксазин)монометин-ціанінперхлорат (ціаніко-вий)	зелений порошок, $l \leq 200$мк	7560. CH_2CH_2OH	?	0	—	$d_{ij}^{2\omega} = 0$	—
39	3.3'-діетил-9,11-(β-карбомі-дотриметилен)-тіадикарбо-ціанінйодид (ціаніновий)	зелені кристаліти з металевим блиском, $l \leq 0,5$ мм	6520. CH_2CH_2OH	?	0	—	$d_{ij}^{2\omega} = 0$	—
40	йодметилат 2-{[2'(3"-метил-бензтіазолініліден - 2" - ме-тил) - тіапіраниліден - 4']ме-тил.)бензтіазол (ціаніно-вий)	темновелений порошок, $l \leq 100$ мк	6620. CH_2CH_2OH	?	0,05	—	—	—
41	Мероціанін (мероціаніно-вий)	темновелений порошок, $l \leq 0,5$ мм	6940. CH_2CH_2OH	?	0	—	$d_{ij}^{2\omega} = 0$	—

(42) * Нижче наведені формули тільки маловідомих сполук.
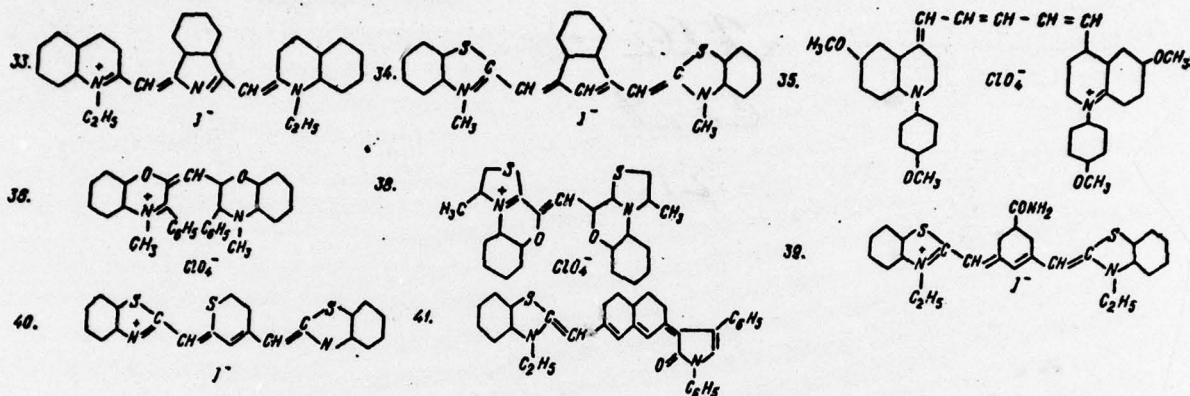
Key: (38c) Bis(1-methylthiazole [2, 3-c] [1, 4] benzoxazine) monomethine cyanine perchlorate (cyanine); (38d) Green powder;(39c) 3,3'-diethyl-9, 11 -(β-carbomidetrimethylene)-thiadicarbocyanineiodide (cyanine); (39d) Green crystallites with metallic luster; (40c) Iodomethylate 2-{[2'(3"-methylbenzothiasoliniliden-2"-methyl) -thiapiraniliden-4']methyl benzothiazol (cyanine); (40d) Dark-green powder; (41c) Merocyanine; (42) *Formulas for lesser known compounds are shown below.

Summary

An experimental study was carried out of the second-harmonic generation (SHG) of the neodymium optical quantum laser by crystalline powders of complex organic compounds. As a result of studying non-linear powder properties of about 200 organic compounds, there were found above 20 substances, the efficiency of which in SHG is not less or surpass that of lithium niobate powder. The experimental results obtained are compared with the data on piezoeffect and structure of molecules and crystals of the investigated compounds. Absorption at the optical quantum laser frequencies ω and 2ω and the substance amorphous state are shown to be basic reasons as a result of which the compounds with a piezoelectric tensor differing from zero generate second harmonic with a disappearing low efficiency. It is marked that though the tensor of the third rank non-linear susceptibility differing from zero most often is characteristic of complex low-symmetrical molecule crystals, because of complicaty of growing large single crystals of such compounds, relatively simple ones such as benzophenone, xanthone, resorcinol. m-nitrobenaldehyde and similar may be of practical importance.

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